

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau(43) International Publication Date
7 August 2003 (07.08.2003)

PCT

(10) International Publication Number
WO 03/064323 A1(51) International Patent Classification²: C01D 3/06, 3/16, C01F 11/46

(74) Agent: GABRIEL, DEVADUSS, CALAB, KUMARAN & SAGAR, 84-C, C6 Lane, Off Central Avenue, Saipik Farms, 110 062 New Delhi (IN).

(21) International Application Number: PCT/IN02/00018

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, IR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LZ, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.

(22) International Filing Date: 31 January 2002 (31.01.2002)

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SI, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BB, CH, CY, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CI, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

(25) Filing Language: English

Declaration under Rule 4.17:

(26) Publication Language: English

as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii)) for the following designations AE, AG, AL, AM, AT, AU, AZ, BA, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, IR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LZ, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZM, ZW, ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SI, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CI, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG)

Published:

- with International search report
- with amended claims

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 03/064323 A1

(54) Title: A PROCESS FOR RECOVERY OF LOW SODIUM SALT FROM BITTERN

(57) Abstract: A new process for recovery of Low Sodium Salt from bittern has been described in the present invention, the said process comprising desulphurization of bittern (by-product of salt industry), evaporation of bittern in solar pans and processing of solid mixture with water to produce a mixture of sodium and potassium chlorides and optionally preparing "tree flowing" and iodized, by known techniques.

WO 03/064323

PCT/IN02/00018

A PROCESS FOR RECOVERY OF LOW SODIUM SALT FROM BITTERN

Field of the invention

The present invention relates to a process for recovery of low sodium salt from bittern in a cost-effective manner. Low sodium salt is primarily a mixture of sodium chloride and potassium chloride and is useful for those persons who have been advised to eat less common salt because of medical conditions like hypertension.

Background and prior art references

It is known that potassium salt—a mineral found in many fruits, vegetables and legumes such as dried peas and beans—may protect against high blood pressure. Presence of potassium in low sodium salt inhibits sodium-induced hypertension. Reference may be made to "The Heinz Handbook of Nutrition" by Benjamin T. Burton, published for H. J. Heinz Co., by McGraw Hill Book Co. Second Edition, page 132-133, wherein it is mentioned that the dietary need for potassium roughly equals that of sodium. It is also stated that muscular weakness, increased nervousness and irritability, mental disorientation and cardiac irregularities manifest potassium deficiency. Many people, especially in poorer countries, do not have access to sufficient amounts of fresh fruits and vegetables with the result that their dietary needs of potassium have to be met by alternative means.

20

Since salt is being taken by people almost daily and it is consumed only in very limited quantity, it is an excellent carrier for micronutrients, an important example being iodised salt. Likewise, salt can be enriched with potassium chloride to provide the essential dietary needs. As a result, low sodium salt is gaining popularity although in most cases potassium content in the salt tends to be low. This is partly because of high cost of food grade potassium chloride, increases total cost of the product (see Table 1) thereby making it unaffordable to many.

Reference may be made to Alves de Lima et al. in patent no. BR 9806380 A, 12 September 2000, entitled "Production of dietetic salt by mixing", wherein it is stated that low sodium dietetic salt is produced by mixing sea salt with potassium chloride, potassium iodate and sodium aluminium silicate, thereby mixing 4 parts of sodium chloride with 6 parts of potassium chloride. The drawback of this process is that one has to separately procure sodium chloride and potassium chloride and blend them together so as to make a solid mixture and also it is difficult to prepare a truly solid homogeneous mixture.

WO 03/064323

PCT/IN02/00018

2

Reference may also be made to Shuqing Wang in patent no. CN 1271541 A, 1 November, 2000, entitled "Multi-element low-sodium nutritive salt", who disclosed the preparation of low sodium nutritive salt by crystallising salt from saturated brine under vacuum. The salt is then mixed uniformly with salts like KCl and MgSO₄.7H₂O, followed by mixing with 5 KIO₃ and Na₂SeO₃ solutions, drying and finally mixing with active Ca and Zn lactate. The drawback of this process is that apart from the difficulty of mixing various constituents in a homogeneous solid mixture, salt is to be crystallised from hot saturated brine involving high energy consumption thereby increasing the cost of production.

10 **Objects of the invention**

The main object of the present invention is to provide a process for recovery of low sodium salt from bittern, which obviates the drawbacks as detailed above.

Another object of the present invention is to undertake such recovery through intermediate 15 formation of crude carnallite which is a mixture of NaCl and the double salt [KCl.MgCl₂.6H₂O] of KCl and MgCl₂. Crude carnallite can be obtained from low sulphate-containing bittern which may, in turn, be produced from naturally occurring brines of low sulphate content or can be obtained even from high sulphate-containing 20 bitterns such as that obtained from sea brine or sub-soil brine through the desulphatation process described in the pending PCT patent Application No. PCT/IN01/00185 dated 22 October, 2001.

Yet another object of the present invention is to vary the composition of crude carnallite in 25 solar pans such that NaCl and KCl in the final composition can be varied as per requirement.

Yet another object of the present invention is to show that valuable nutrients like calcium and magnesium can be introduced into the salt directly from bittern and there is no need of external addition of these nutrients.

30

Yet another object of the present invention is to prepare low sodium salt under ambient conditions of processing except the final drying of product in an oven.

Yet another object of the present invention is to treat low sodium salt with suitable 35 additives to impart free flowing properties to the salt and for iodisation of the salt by known methods.

WO 03/064323

PCT/IN02/00018

3

SUMMARY OF THE PRESENT INVENTION

The present invention relates to recovery of low sodium salt from bittern which is a by-product of salt industry. The process involves treatment of bittern with calcium chloride to precipitate calcium sulphate, solar evaporation of desulphated bittern in crystallisers to produce a solid mixture of sodium chloride and carnallite and processing the said mixture with water to produce low sodium salt. This is dried and treated with additives to give free flowing properties. In a variation of the process, brine can be desulphated prior to crystallization of common salt as described in the pending PCT patent Application No. 10 PCT/IN01/00185 dated 22 October, 2001.

Accordingly the present invention provides a process for the preparation of low sodium salt which comprises (i) treatment of bittern of density 29 °Be' to 30 °Be' containing sulphate in the range of 20 to 65 g/L with calcium chloride—which is obtained from any of the sources/methods described in the pending PCT patent Application No. 15 PCT/IN01/00185 dated 22 October, 2001, with concentration of calcium chloride ranging from 80 g/L to 450 g/L and in the mol ratio of 0.9 to 1.1 moles of calcium chloride to one mole of sulphate in bittern to produce calcium sulphate; (ii) separating calcium sulphate from desulphated bittern; (iii) evaporating desulphated bittern containing 90 to 135 g/L of 20 sodium chloride and 20 to 25 g/L of potassium chloride, in solar pans till density ranging from 30 to 33.0 °Be' is reached, with deposition of excess salt, in pans; (iv) separating excess salt from concentrated bittern by decantation; (v) evaporating further this bittern in a second set of solar pans till density of 35.5 °Be' is reached, with deposition of the desired mixture of sodium chloride and carnallite ($KCl \cdot MgCl_2 \cdot 6H_2O$), in pans; (vi) 25 scraping and heaping the solid mixture and draining out the mother liquor; (vii) treating solid mixture with water in the ratio of 0.3 to 0.5 parts of water with one part of solid mixture in a stirred vessel for a period in the range of 20 to 60 minutes thereby producing a solid, which is low sodium salt, and a liquid in equilibrium with this solid; (viii) separating the solid product from the liquid in a centrifuge; (ix) recycling the liquid containing 30 dissolved magnesium chloride and 30 to 55 g/L of sodium and potassium chlorides to carnallite pans for enhanced recovery of sodium and potassium salts; (x) drying low sodium salt at a temperature ranging from 90 °C to 130 °C by known techniques; (xi) treating dried material with 25 to 50 ppm of potassium iodate and 0.01 % to 0.05 % w/w light magnesium carbonate or *in situ* generating magnesium carbonate from the reaction of 35 sodium carbonate and residual $MgCl_2$ in the salt in order to make the material free flowing.

WO 03/064323

PCT/IN02/00018

4

In an embodiment of the present invention bittern is treated with required quantity of calcium chloride such that the concentration of sulphate in bittern of 29-30 °Be' after treatment is reduced to the levels of 1-15 g/L to promote carnallite formation.

5 In yet another embodiment of the present invention desulphated bittern may be evaporated in solar pans for adequate period till density reaches to a levels in the range of 30 to 33 °Be' when excess salt is separated from concentrated bittern.

10 In yet another embodiment of the present invention, the desulphated bittern may be further evaporated in solar pans for adequate period till the density to a levcls in the range of 34.5 °Be' to 36 °Be' is reached thereby depositing a mixture containing sodium chloride and carnallite.

15 In yet another embodiment of the present invention, the solid mixture is treated with 0.3-0.5 kg water/kg of crude solid mixture to decompose the carnallite and the resultant dry solid, free from liquid, is obtained by centrifugation and subsequent oven drying.

20 In yet another embodiment of the present invention, the solid composition of NaCl/KCl is treated by known techniques with appropriate micronutrient additives and free flow aids as required to impart the final desired characteristics to the product.

DESCRIPTION OF THE INVENTION

25 Bittern, a by-product of salt industry, having a density of 29-30 °Be' is treated with calcium chloride as described in the pending PCT patent application No. PCT/IN01/00185 dated 22 October, 2001.

30 Desulphated bittern is taken into a solar pan where it undergoes evaporation with the deposition of common salt and density of bittern is raised. The density to which bittern is required to be raised depends upon quantity of excess salt required to be removed by solar evaporation which further depends upon the desired composition of potassium chloride and sodium chloride in the final product. This composition may range from 20 % KCl to 70 % KCl which is equivalent to density of bittern in this crystalliser to be in the range from 30.5°Be' to 33°Be'. After removal of excess salt bittern is taken to carnallite crystalliser pans where mixture of carnallite ($KClMgCl_2 \cdot 6H_2O$) and sodium chloride crystallises out in the density range 33 to 36°Be'.

WO 03/064323

PCT/IN02/00018

5

The mixture of carnallite double salt and sodium chloride is treated with 0.3-0.5 kg water/kg of solid mixture in a stirred vessel as per known procedure to decompose the double salt and produce a solid mixture of sodium chloride and potassium chloride. The solid-liquid mixture is centrifuged and the supernatant liquid, comprising mainly $MgCl_2$ and some (30-55 g/L) dissolved potassium chloride and sodium chloride is recycled to the carnallite pan to recover residual quantity of potassium chloride and sodium chloride.

5 The solid residue obtained after centrifugation is dried in a tray drier at a temperature between 90-130 °C, treated with 0.01-0.05 % light magnesium carbonate (100-150 g/L density) and dried to make the same free flowing. If required, the low sodium salt may be iodised with aqueous KIO_3 solution (10-50 ppm I) to make it saleable as free flowing iodised low sodium salt.

10 In the field of chemical technology the recovery of low sodium salt from bittern, a by-product of salt industry, has assumed importance on account of its nutritive value. The process involves chemical treatment of bittern with $CaCl_2$ -containing distiller by-product waste of soda ash industry or pure calcium chloride, to separate sulphate; concentrating bittern in solar pans to produce mixture of salt and carnallite and finally processing the mixture to produce low sodium salt. This salt is optionally made free flowing and iodised 15 with suitable additives.

15 The present invention discloses the preparation of low sodium salt containing different proportions of NaCl and KCl directly from brine/bittern in solar pans and it obviates the need of any external addition of food grade KCl and other nutrients in salt. The inventive steps adopted in the present invention are: (i) realization that desulphated bittern of density 29-30 °Be' that yields a mixture of sodium chloride and carnallite upon further evaporation can be a source for recovery of low sodium salt directly, (ii) control of bittern density of desulphated bittern and charging of carnallite pan in a manner so as to adjust NaCl content in crude carnallite mixture, (iii) decomposition of the double salt in the solid mixture in a 20 manner so as to achieve the NaCl/KCl mixture of desired ratio with highest possible yield, (iv) simple method of industrial centrifugation to yield low sodium salt composition with desired purity without any need for washing of the solid, and (v) recycling of the supernatant into carnallite pan so as to maximize yield of low sodium salt from given 25 quantity of bittern.

WO 03/064323

PCT/IN02/00018

6

The following examples are given by way of illustration and therefore should not be construed to limit the scope of the present invention.

Example 1

5 In this example 35 L of bittern of subsoil source, with density 29 °Be' and having the following chemical analysis: $Mg^{2+} = 48.0 \text{ g/L}$; $Ca^{2+} = 0.5 \text{ g/L}$; $Na^+ = 37 \text{ g/L}$ (95 g/L as NaCl); $K^+ = 11.2 \text{ g/L}$ (21.5 g/L as KCl); $Cl^- = 191.1 \text{ g/L}$; $SO_4^{2-} = 26.7 \text{ g/L}$ (0.278 M) was used for the production of low sodium salt. This bittern containing 9.73 moles of SO_4^{2-} was desulphated by using 9.75 moles of Ca^{2+} [(2.46 L of calcium chloride solution obtained by dissolution of limestone and hydrochloric acid) containing 440 g/L CaCl₂]. After removal of gypsum, desulphated bittern is evaporated to a density of 35.5 °Be'. 7 kg of crude carnallite containing a mixture of sodium chloride and carnallite was separated out. Crude carnallite had the following chemical composition: $Mg^{2+} = 5.46 \%$; $Ca^{2+} = 0.35 \%$; $Na^+ = 16.69 \%$ (42.09 % as NaCl); $K^+ = 5.26 \%$ (10.05 % as KCl); $Cl^- = 47.49 \%$; $SO_4^{2-} = 0.38 \%$; $H_2O = 24.4 \%$.

10

15

The total material was treated with 2.8 L of water in a stirred vessel and stirring continued for 30 min. The supernatant solution was decanted and the solid residue, weighing 2.61 kg, had the following chemical analysis after filtration: $Mg^{2+} = 0.52 \%$; $Ca^{2+} = 0.55 \%$; $SO_4^{2-} = 0.4 \%$; $NaCl = 76.1 \%$; $KCl = 21.5 \%$.

20

The volume of the supernatant was 4.02 L and contained mainly MgCl₂ besides small quantities of NaCl and KCl. This liquid is evaporated to 35.5 °Be' and the carnallite obtained was processed in similar manner as above to obtain an additional 0.4 kg of low sodium salt. Overall recovery on KCl basis worked out to be nearly 87 %.

25

Example 2

In this example the experiment was conducted in the field using bittern of sub-soil origin and utilising solar energy for evaporation in shallow pans lined with thin gauge plastic to avoid percolation loss. 1500 L of the bittern of Example 1 having total sulphate content of 30 417 moles was processed for this purpose. The bittern was desulphated using sulphate equivalent of calcium chloride solution of concentration as in Example 1. After removal of gypsum, the desulphated bittern was added into solar pans and left for evaporation up to 32.5 °Be'. The bittern is allowed to evaporate further in a second pan where a mixture of carnallite and sodium chloride weighing 205 kg is deposited at a liquid density of 35.5 °Be'. This mixture had the following chemical analysis of the main components: $Mg^{2+} = 7.81 \%$; $Na^+ = 6.34 \%$; $K^+ = 7.37 \%$; $Cl^- = 39.38 \%$.

35

WO 03/064323

PCT/IN02/00018

7

The above solid after separation from end bittern is treated with 82 L of water in a stirred vessel for one hour and centrifuged when practically the entire magnesium goes into the supernatant liquid (180 L) along with some fraction of sodium and potassium chlorides, and 55 kg of low sodium salt of following composition is obtained: $Mg^{2+} = 0.57\%$; $Ca^{2+} = 0.35\%$; $SO_4^{2-} = 0.25\%$; $NaCl = 53.58\%$; $KCl = 44.52\%$.

The supernatant liquid is evaporated in solar pans in similar manner as in Example 1 and solid deposited is processed with water as before to recover 6.0 kg of additional low sodium salt giving a total yield of 61 kg.

10

Example 3

In this example high sulphate bittern of sea water origin was used for low sodium salt preparation. Chemical analysis of this bittern is given below: $Mg^{2+} = 50.45\text{ g/L}$; $Ca^{2+} = 0.41\text{ g/L}$; $Na^+ = 37.39\text{ g/L}$ (95 g/L as NaCl); $K^+ = 13.90\text{ g/L}$ (26.5 g/L as KCl); $Cl^- = 167.33\text{ g/L}$; $SO_4^{2-} = 66.80\text{ g/L}$.

Bittern was desulphated with calcium chloride obtained as liquid distiller by-product from soda ash industry. Analysis of the liquid by-product is given below: Water = 834 g/L; $Na^+ = 26.03\text{ g/L}$; $Ca^{2+} = 55.47\text{ g/L}$; $Cl^- = 132.4\text{ g/L}$; $OH^- = 2.8\text{ g/L}$; $CaCO_3 = 9.96\text{ g/L}$; $CaSO_4 = 2.49\text{ g/L}$; $MgO = 3.74\text{ g/L}$. The above distiller by-product was settled to remove suspended impurities and a clear liquid supernatant was obtained containing 66 g/L and 128.7 g/L NaCl and CaCl₂, respectively.

1500 L of 29 °Be' bittern (containing a total of 1044 moles SO_4^{2-}) was treated with 900 L of the settled distiller by-product (containing a total of 1044 moles CaCl₂) in a plastic-lined solar pan. Mixed liquid was allowed to evaporate in the pan, to ensure complete deposition of calcium sulphate till density of 29 °Be' was achieved again. Clear liquid from mixing pan was transferred to second pan which was also lined with plastic lining and was allowed to evaporate till liquid density of 35.5 °Be' as achieved. 300 kg of solid which was a mixture of sodium chloride and carnallite was separated from end bittern. The chemical analysis of solid mixture is given below: $Mg^{2+} = 6.0\%$; $Ca^{2+} = 0.35\%$; $SO_4^{2-} = 0.4\%$; $Na^+ = 16.31\%$ (41.45 % as NaCl); $K^+ = 5.79\%$ (11.05 % as KCl). The solid mixture was treated with 135 L of water in a stirred vessel for one hour and centrifuged. 240 L of supernatant liquid and 120 kg of low sodium salt with the composition: $Mg^{2+} = 0.3\%$; $Ca^{2+} = 0.4\%$; $NaCl = 74.3\%$; $KCl = 22.2\%$ were obtained.

WO 03/064323

PCT/IN02/00018

8

Example 4

In this example low sodium salt as produced above was treated with potassium iodate and light magnesium carbonate in order to provide free flowing properties to salt. Accordingly 60 kg of low sodium salt was first dried at 110 °C and after pulverisation was treated with 5 3 g of potassium iodate (in the form of a 10 % solution), followed by 12 g of light magnesium carbonate and was immediately packed tightly in bags.

The main advantages of the present invention are:

- (1) The homogeneous mixture of sodium chloride and potassium chloride, which constitutes low sodium salt, can be produced directly from 29-30 °Be' bittern instead of producing such salt through artificial mixing of the two solids as presently undertaken.
- (2) The ratio of potassium chloride and sodium chloride can be adjusted in the range from 20 % KCl to 70 % KCl according to customer requirements by varying the baume density at which the carnallite crystalliser pan is charged.
- (3) The process involves no heating or cooling except final drying of product in an oven and the production of crude carnallite is carried out under ambient conditions with the help of solar energy while subsequent processing of the carnallite for recovery of low sodium salt is also carried out under ambient conditions.
- (4) Other nutrients like calcium and magnesium which are beneficial in small amounts are drawn from bittern itself and need not be added from outside.
- (5) The supernatant liquor remaining after formation of low sodium salt can be recycled in the carnallite pan to boost yield of the process.
- (6) A variety of calcium ion-containing raw material can be used for the desulphatation of bittern required for carnallite production when the bittern contains high levels of sulphate.
- (7) Compared to the high cost of production of low sodium salt by conventional route as shown in Table 1, the low sodium salt can be produced at considerably lower cost by the method of the present invention, especially when produced from sub-soil bittern as illustrated in Table 2 and/or when distiller by-product of soda ash industry, after clarification, is used as calcium chloride source which would greatly reduce the calcium chloride raw material cost in Table 2 and/or when low sodium salt is produced by salt manufacturers who would have bittern available at no cost since it is mostly being discharged as waste.

WO 03/064323

PCT/IN02/00018

9

Table 1

**ESTIMATED COST OF PRODUCTION FOR 3000 TONS/ANNUM LOW SODIUM SALT
BYCONVENTIONAL PROCESS OF MIXING NaCl and KCl (55% NaCl; 45 % KCL)**

5

Raw Material	Quantity Required/t on	Rate in Indian Rupees/ton	Annual cost in Rupees/M
Sodium Chloride	1650	1,000	1.65
Potassium Chloride (Food grade)	1350	20,000	27.00
<u>Other costs</u>		1,000	3.00
(including cost of mixing, depreciation on machinery, etc)			
<u>Total cost for 3000 tons</u>			<u>31.65</u>
Cost of production per ton			Rs.10,550

WO 03/064323

PCT/IN02/00018

10

Table 2

**ESTIMATED COST OF PRODUCTION FOR 3000 TONS/ANNUM LOW SODIUM
SALT (55 % NaCl; 45 % KCL) FROM SUB-SOIL AND SEA BITTERNS UNDER
INDIAN CONDITIONS**

Raw Material	Quantity required	Rate	Cost in Rs./M
Bittern	80,000 M ³	2.4	
Calcium chloride (on CaCl ₂ .2H ₂ O basis)	2400 tons (sub-soil bittern) 6000 tons (sea bittern)	3500/ton "	8.40 21.00
Utilities			
Power	3,55,200 KWH	@ Rs. 4/- KWH	1.42
LDO for drying Water	12,223 L 8,000 m ³	@ Rs.18/L @ Rs.20/m ³	0.22 0.16
Field Labour	5,500 mandays	@ Rs. 75/ manday	0.42
Supervisory Staff			0.30
Other costs			
Depreciation on plant and machinery (Without liner)			0.35
Repair/replacement cost of liner for carnallite pan (assuming the life of liner to be 2years)			0.75
Interest on capital investment		@ 12% per annum	0.66
Total cost (Rs/M) (Sub-soil bittern) (Sea bittern)			15.08 27.68
Cost of Low Sodium Salt per ton			(in Rupees)
From Sub-soil bittern			5027
From Sea bittern			9227

WO 03/064323

PCT/IN02/00018

11

CLAIMS

1. An economical process for recovery of low-sodium salt, preparing free flowing low-sodium salt or optionally preparing iodized low sodium salt and with enhanced recovery of low sodium salt from bittern, the said process comprising steps of:
 - a) treating the bittern with calcium chloride solution to produce insoluble calcium sulfate,
 - b) separating calcium sulfate of step (a) to obtain desulphated bittern,
 - c) evaporating the desulphated bittern of step (b) in solar pans with deposition of excess salt in pans,
 - d) removing the excess salt deposit of step (c) to obtain concentrated desulphated bittern,
 - e) feeding the concentrated desulphated bittern of step (d) to a carnallite pans and continuing the solar evaporation till solid deposition is initiated,
 - f) separating the solid mixture of step (e) constituting a mixture of sodium chloride and carnallite ($KClMgCl_2 \cdot 6H_2O$) from end bittern,
 - g) treating with stirring the solid mixture of step (f) with water over a period of 20-60 minutes to produce desired sodium salt composition and a liquid in equilibrium with this solid containing mainly magnesium chloride with dissolved sodium chloride and potassium chloride,
 - h) separating the solid product of step (g) from the liquid by centrifugation, and
 - i) drying the solid of step (h) at a temperature ranging from 90° - 130° C to obtain low sodium salt.
2. The process as claimed in claim 1, wherein treating the low-sodium salt of step (i) with an additive to obtain free flowing low sodium salt.
3. The process as claimed in claim 1, wherein treating low-sodium of step (i) with an alkali iodate salt to obtain iodized low sodium salt.
4. The process as claimed in claim 1, wherein recovery of low-sodium salt can be enhanced by recycling the bittern of step (h).
5. A process as claimed in claim 1, wherein the low sodium salt can be produced directly from 29-30° Be bittern containing sodium chloride, potassium chloride and Mg^{2+} .
6. A process as claimed in claim 1, wherein the source for bittern can be from seawater or sub soil origin and preferably bittern having low sulphate content.

WO 03/064323

PCT/IN02/00018

12

7. A process as claimed in claim 1, wherein in step (a) the concentration of calcium chloride solution used is in the range of 80 to 450 g/liter.
8. A process as claimed in claim 1 wherein in step (a) the source of calcium chloride is from distiller by product waste of soda ash industry.
9. A process as claimed in claim 1, wherein in step (b) the desulphated bittern has a concentration of sodium chloride 90 – 135 g/liter and potassium chloride 20-25 g/liter.
10. A process as claimed in claim 1, wherein in step (c) the evaporation of desulphated bittern in solar pans is performed to obtain concentrated desulphated bittern of density ranging from 30-33° Be.
11. A process as claimed in claim 1, wherein in step (c) the potassium chloride and sodium chloride can be adjusted in the range of 20% KCl to 70% KCl by varying between 30 to 33° Be the density of desulphated bittern.
12. A process as claimed in claim 1, wherein in step (e) the evaporation of concentrated desulphated bittern is performed to achieve a density of 35.5° Be.
13. A process as claimed in claim 1, wherein in step (g) the ratio of water to the solid mixture ranges from 0.30-0.50 to 1.00.
14. A process as claimed in claim 1, wherein in steps (a to h) are carried out at an ambient temperature and step (i) is carried out at a temperature range of 90° - 130°C.
15. A process as claimed in claim 1, wherein in step (j) the additive used is light magnesium carbonate at a concentration range of 0.01 – 0.05% w/w with respect to low-sodium salt.
16. A process as claimed in claim 1, wherein in step (k) the alkali salt used is potassium iodate at a concentration range of 10-50 ppm with respect to low sodium salt.
17. A process as claimed in claim 1, wherein in step (l) the supernatant liquor of step (h) remaining after decomposing of crude carnallite of step (f) can be recycled in carnallite pan to increase yield of the process to 87-90% based on potassium content of the bittern used.
18. A process as claimed in claim 1, wherein each nutrient calcium and magnesium ranging in the amount 0.01 to 2.0% is drawn from the bittern used and not to be externally added.

WO 03/064323

PCT/IN02/00018

13

19. A process as claimed in claim 1, wherein the isolated yield of low sodium salt from bittern is in the range of 0.03 kg/litre to 0.07 kg/litre.
20. A process as claimed in claim 1, wherein the isolated yield of low sodium salt from bittern after adopting recycling process is in the range of .04 kg/lt to 0.09 kg/lt.

5

WO 03/064323

PCT/IN02/00018

14

AMENDED CLAIMS

[received by the International Bureau on 26 November 2002 (26.11.02);
Claims 2, 3 and 4 amended. Remaining claims unchanged. (3 pages)]

1. An economical process for recovery of low-sodium salt, preparing free flowing low-sodium salt or optionally preparing iodized low sodium salt and with enhanced recovery of low sodium salt from bittern, the said process comprising steps of:
 - a) treating the bittern with calcium chloride solution to produce insoluble calcium sulfate,
 - b) separating calcium sulfate of step (a) to obtain desulphated bittern,
 - c) evaporating the desulphated bittern of step (b) in solar pans with deposition of excess salt in pans,
 - d) removing the excess salt deposit of step (c) to obtain concentrated desulphated bittern,
 - e) feeding the concentrated desulphated bittern of step (d) to a carnallite pans and continuing the solar evaporation till solid deposition is initiated,
 - f) separating the solid mixture of step (e) constituting a mixture of sodium chloride and carnallite ($KCl \cdot MgCl_2 \cdot 6H_2O$) from end bittern,
 - g) treating with stirring the solid mixture of step (f) with water over a period of 20-60 minutes to produce desired sodium salt composition and a liquid in equilibrium with this solid containing mainly magnesium chloride with dissolved sodium chloride and potassium chloride,
 - h) separating the solid product of step (g) from the liquid by centrifugation, and
 - i) drying the solid of step (h) at a temperature ranging from 90° - 130° C to obtain low sodium salt,
2. A process as claimed in claim 1, wherein treating the low-sodium salt of step (i) with an additive to obtain free flowing low sodium salt.
3. A process as claimed in claim 1, wherein treating low-sodium of step (i) with an alkali iodate salt to obtain iodized low sodium salt.
4. A process as claimed in claim 1, wherein recovery of low-sodium salt can be enhanced by recycling the bittern of step (h).

AMENDED SHEET (ARTICLE 19)

WO 03/064323

PCT/IN02/00018

15

5. A process as claimed in claim 1, wherein the low sodium salt can be produced directly from 29-30° Be bittern containing sodium chloride, potassium chloride and Mg²⁺.
6. A process as claimed in claim 1, wherein the source for bittern can be from seawater or sub soil origin and preferably bittern having low sulphate content.
7. A process as claimed in claim 1, wherein in step (a) the concentration of calcium chloride solution used is in the range of 80 to 450 g/liter.
8. A process as claimed in claim 1 wherein in step (a) the source of calcium chloride is from distiller by product waste of soda ash industry.
9. A process as claimed in claim 1, wherein in step (b) the desulphated bittern has a concentration of sodium chloride 90 – 135 g/liter and potassium chloride 20-25 g/liter.
10. A process as claimed in claim 1, wherein in step (c) the evaporation of desulphated bittern in solar pans is performed to obtain concentrated desulphated bittern of density ranging from 30-33° Be.
11. A process as claimed in claim 1, wherein in step (c) the potassium chloride and sodium chloride can be adjusted in the range of 20% KCl to 70% KCl by varying between 30 to 33° Be the density of desulphated bittern.
12. A process as claimed in claim 1, wherein in step (e) the evaporation of concentrated desulphated bittern is performed to achieve a density of 35.5° Be.
13. A process as claimed in claim 1, wherein in step (g) the ratio of water to the solid mixture ranges from 0.30-0.50 to 1.00.
14. A process as claimed in claim 1, wherein in steps (a to h) are carried out at an ambient temperature and step (i) is carried out at a temperature range of 90° - 130°C.
15. A process as claimed in claim 1, wherein in step (j) the additive used is light magnesium carbonate at a concentration range of 0.01 – 0.05% w/w with respect to low-sodium salt.
16. A process as claimed in claim 1, wherein in step (k) the alkali salt used is potassium iodate at a concentration range of 10-50 ppm with respect to low sodium salt.

AMENDED SHEET (ARTICLE 19)

WO 03/064323

PCT/IN02/00018

16

17. A process as claimed in claim 1, wherein in step (l) the supernatant liquor of step (h) remaining after decomposing of crude carnallite of step (f) can be recycled in carnallite pan to increase yield of the process to 87-90% based on potassium content of the bittern used.
18. A process as claimed in claim 1, wherein each nutrient calcium and magnesium ranging in the amount 0.01 to 2.0% is drawn from the bittern used and not to be externally added.
19. A process as claimed in claim 1, wherein the isolated yield of low sodium salt from bittern is in the range of 0.03 kg/litre to 0.07 kg/litre.
20. A process as claimed in claim 1, wherein the isolated yield of low sodium salt from bittern after adopting recycling process is in the range of .04 kg/lt to 0.09 kg/lt.

AMENDED SHEET (ARTICLE 19)

INTERNATIONAL SEARCH REPORT		National Application No PCT/IN 02/00018
A. CLASSIFICATION OF SUBJECT MATTER IPC 7 C01D3/06 C01D3/16 C01F11/46		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 7 C01D C01F		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) WPI Data, EPO-Internal, PAJ, CHEM ABS Data, COMPENDEX, INSPEC		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 099 528 A (PABLO HADZERIGA) 30 July 1963 (1963-07-30) claims 1-6 column 1, line 65 -column 2, line 4 column 2, line 12-15 column 2, line 48 -column 3, line 47 --- GB 1 142 901 A (ALFRED FREDERICK NYLANDER) 12 February 1969 (1969-02-12) claims 1,2 page 5, line 59 -page 6, line 78 figure 5 examples ---	1-20
Y		1-20
		-/-
<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C.		<input checked="" type="checkbox"/> Patent family members are listed in annex.
* Special categories of cited documents : "A" document relating the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the International filing date "L" document which may throw doubt on priority, claim(s) or which is cited to establish the publication date of another citation or other specific reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the International filing date but later than the priority date claimed		
Date of the actual compilation of the international search 18 September 2002		Date of mailing of the international search report 26/09/2002
Name and mailing address of the ISA European Patent Office, P.O. Box 8018 Patentlaan 2 NL - 2280 HV Rijswijk Tel (+31-70) 340-2040, Tx. 31 651 epo nl Fax (+31-70) 340-3016		Authorized officer Rhodes, K

Form PCT/AS/210 (second sheet) (July 1992)

AMENDED SHEET (ARTICLE 19)

INTERNATIONAL SEARCH REPORT		International Application No PCT/IN 02/00018
C(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No,
Y	US 3 536 444 A (NYLANDER ALFRED F) 27 October 1970 (1970-10-27) claims 1,2 column 6, line 55 -column 8, line 22 figure 5 examples	1-20
Y	GB 1 500 288 A (CANADIAN IND) 8 February 1978 (1978-02-08) claim 1 page 1, line 58,59	1-20
A	PATENT ABSTRACTS OF JAPAN vol. 014, no. 171 (C-0706), 3 April 1990 (1990-04-03) & JP 02 022122 A (NAIKAI ENGIYOU KK;OTHERS: 01), 25 January 1990 (1990-01-25) abstract	1-20

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

Int'l Application No
PCT/IN 02/00018

Patent document cited in search report		Publication date		Patent family member(s)		Publication date
US 3099528	A	30-07-1963	NONE			
GB 1142901	A	12-02-1969	FR	1471300 A		03-03-1967
US 3536444	A	27-10-1970	NONE			
GB 1500288	A	08-02-1978	AU BE DE FR LU NL	8129675 A 829214 A1 2522509 A1 2272035 A1 72529 A1 7505788 A		25-11-1976 15-09-1975 04-12-1975 19-12-1975 08-10-1975 25-11-1975
JP 02022122	A	25-01-1990	NONE			

Form PCT/ISA/210 (patent family annex) (July 1992)

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
7 August 2003 (07.08.2003)

PCT

(10) International Publication Number
WO 03/064323 A1

(51) International Patent Classification?: C01D 3/06, 3/16, C01F 11/46

(21) International Application Number: PCT/IN02/00018

(22) International Filing Date: 31 January 2002 (31.01.2002)

(25) Filing Language: English

(26) Publication Language: English

(71) Applicant (for all designated States except US): COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH [IN/IN]; Rali Marg, 110 001 New Delhi (IN).

(72) Inventors; and

(75) Inventors/Applicants (for US only): VOJRA, Rajinder, Nath [IN/IN]; Central Salt and Marine Chemicals Research Institute, Gijuhbai Badhetea Marg, Bhavnagar, 364 002 Gujarat (IN). GHOSH, Pushpito, Kumar [IN/IN]; Central Salt and Marine Chemicals Research Institute, Gijuhbai Badhetea Marg, Bhavnagar, 364 002 Gujarat (IN). GANDHI, Maheshkumar, Ramniklal [IN/IN]; Central Salt and Marine Chemicals Research Institute, Gijuhbai Badhetea Marg, Bhavnagar, 364 002 Gujarat (IN). DERIYA, Hasina, Hajibhai [IN/IN]; Central Salt and Marine Chemicals Research Institute, Gijuhbai Badhetea Marg, Bhavnagar, 364 002 Gujarat (IN). DAVE, Rohit, Harshadray [IN/IN]; Central Salt and Marine Chemicals Research Institute, Gijuhbai Badhetea Marg, Bhavnagar, 364 002 Gujarat (IN). HALDER, Knoushik [IN/IN]; Central Salt and Marine Chemicals Research Institute, Gijuhbai Badhetea Marg, Bhavnagar, 364 002 Gujarat (IN). MAJEETHIA, Kishorkumar, Manmohandas [IN/IN]; Central Salt and Marine Chemicals Research Institute, Gijuhbai Badhetea Marg, Bhavnagar, 364 002 Gujarat (IN). DAGA, Sohan, Lal [IN/IN]; Central Salt and Marine Chemicals Research Institute, Gijuhbai Badhetea Marg, Bhavnagar, 364 002 Gujarat (IN).

(74) Agent: GABRIEL, DEVADOSS, CALAB, KUMARAN & SAGAR; 84-C, C6 Lane, Off Central Avenue, Sainik Farms, 110 062 New Delhi (IN).

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, IL, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SI, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KR, LS, MW, MZ, SD, SI, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SI, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declaration under Rule 4.17:

- ... as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(i)) for the following designations AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, IL, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SI, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZM, ZW, ARIPO patent (GH, GM, KR, LS, MW, MZ, SD, SI, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SI, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG)

Published:

- ... with international search report
- ... with amended claims and statement

Date of publication of the amended claims and statement:

13 November 2003

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 03/064323 A1

(54) Title: A PROCESS FOR RECOVERY OF LOW SODIUM SALT FROM BITTERN

(57) Abstract: A new process for recovery of Low Sodium Salt from bittern has been described in the present invention, the said process comprising desulphatation of bittern (by-product of salt industry), evaporation of bittern in solar pans and processing of solid mixture with water to produce a mixture of sodium and potassium chlorides and optionally preparing "free flowing" and iodized, by known techniques.

WO 03/064323

PCT/IN02/00018

14

AMENDED CLAIMS

[received by the International Bureau on 26 November 2002 (26.11.02);
Claims 2, 3 and 4 amended, Remaining claims unchanged. (3 pages)]

1. An economical process for recovery of low-sodium salt, preparing free flowing low-sodium salt or optionally preparing iodized low sodium salt and with enhanced recovery of low sodium salt from bittern, the said process comprising steps of:
 - a) treating the bittern with calcium chloride solution to produce insoluble calcium sulfate,
 - b) separating calcium sulfate of step (a) to obtain desulphated bittern,
 - c) evaporating the desulphated bittern of step (b) in solar pans with deposition of excess salt in pans,
 - d) removing the excess salt deposit of step (c) to obtain concentrated desulphated bittern,
 - e) feeding the concentrated desulphated bittern of step (d) to a carnallite pans and continuing the solar evaporation till solid deposition is initiated,
 - f) separating the solid mixture of step (e) constituting a mixture of sodium chloride and carnallite ($KCl \cdot MgCl_2 \cdot 6H_2O$) from end bittern,
 - g) treating with stirring the solid mixture of step (f) with water over a period of 20-60 minutes to produce desired sodium salt composition and a liquid in equilibrium with this solid containing mainly magnesium chloride with dissolved sodium chloride and potassium chloride,
 - h) separating the solid product of step (g) from the liquid by centrifugation, and
 - i) drying the solid of step (h) at a temperature ranging from 90° - 130° C to obtain low sodium salt.
2. A process as claimed in claim 1, wherein treating the low-sodium salt of step (i) with an additive to obtain free flowing low sodium salt.
3. A process as claimed in claim 1, wherein treating low-sodium of step (i) with an alkali iodate salt to obtain iodized low sodium salt.
4. A process as claimed in claim 1, wherein recovery of low-sodium salt can be enhanced by recycling the bittern of step (b).

AMENDED SHEET (ARTICLE 19)

WO 03/064323

PCT/IN02/00018

15

5. A process as claimed in claim 1, wherein the low sodium salt can be produced directly from 29-30° Be bittern containing sodium chloride, potassium chloride and Mg²⁺.
6. A process as claimed in claim 1, wherein the source for bittern can be from seawater or sub soil origin and preferably bittern having low sulphate content.
7. A process as claimed in claim 1, wherein in step (a) the concentration of calcium chloride solution used is in the range of 80 to 450 g/liter.
8. A process as claimed in claim 1 wherein in step (a) the source of calcium chloride is from distiller by product waste of soda ash industry.
9. A process as claimed in claim 1, wherein in step (b) the desulphated bittern has a concentration of sodium chloride 90 – 135 g/liter and potassium chloride 20-25 g/liter.
10. A process as claimed in claim 1, wherein in step (c) the evaporation of desulphated bittern in solar pans is performed to obtain concentrated desulphated bittern of density ranging from 30-33° Be.
11. A process as claimed in claim 1, wherein in step (c) the potassium chloride and sodium chloride can be adjusted in the range of 20% KCl to 70% KCl by varying between 30 to 33° Be the density of desulphated bittern.
12. A process as claimed in claim 1, wherein in step (c) the evaporation of concentrated desulphated bittern is performed to achieve a density of 35.5° Be.
13. A process as claimed in claim 1, wherein in step (g) the ratio of water to the solid mixture ranges from 0.30-0.50 to 1.00.
14. A process as claimed in claim 1, wherein in steps (a to h) are carried out at an ambient temperature and step (i) is carried out at a temperature range of 90° - 130°C.
15. A process as claimed in claim 1, wherein in step (j) the additive used is light magnesium carbonate at a concentration range of 0.01 – 0.05% w/w with respect to low-sodium salt.
16. A process as claimed in claim 1, wherein in step (k) the alkali salt used is potassium iodate at a concentration range of 10-50 ppm with respect to low sodium salt.

AMENDED SHEET (ARTICLE 19)

WO 03/064323

PCT/IN02/00018

16

17. A process as claimed in claim 1, wherein in step (j) the supernatant liquor of step (h) remaining after decomposing of crude carnallite of step (f) can be recycled in carnallite pan to increase yield of the process to 87-90% based on potassium content of the bittern used.
18. A process as claimed in claim 1, wherein each nutrient calcium and magnesium ranging in the amount 0.01 to 2.0% is drawn from the bittern used and not to be externally added.
19. A process as claimed in claim 1, wherein the isolated yield of low sodium salt from bittern is in the range of 0.03 kg/litre to 0.07 kg/litre.
20. A process as claimed in claim 1, wherein the isolated yield of low sodium salt from bittern after adopting recycling process is in the range of .04 kg/lt to 0.09 kg/lt.

AMENDED SHEET (ARTICLE 19)

WO 03/064323

PCT/IN02/00018

17

Statement under Article 19

IN THE INTERNATIONAL BUREAU OF WIPO

Re: International Application No. PCT/IN02/00018
 Applicant: Council of Scientific and Industrial Research
 International Filing Date: 31 January, 2002 (31-01-2002)
 Title: A Process For Recovery Of Low Sodium Salt From Bittern

With reference to Search Report dated 26 September, 2002, we respectfully submit our response as follows:

We claim present invention as novel with following arguments:

1. The carnallite decomposed product obtained directly from crude carnallite, which is processed to be used as low sodium edible salt is a highly cost-effective and simple process over known prior art methods.
2. That the entire process of making low sodium salt is carried out under ambient conditions.
3. That crude carnallite can be obtained even from high sulphate-containing bittern by carrying out desulphatation of the bittern in a highly cost-effective manner, such as through use of soda ash distiller waste.
4. That the ratio of NaCl and KCl in low sodium salt can be varied conveniently by charging the desulphated bittern into the salt pan for carnallite production at an appropriate bittern density in the range of 30 - 33 °Be. The KCl content increasing with increase of Baume in this range.
5. That nutrients like Calcium and Magnesium in Low sodium salt are drawn from bittern itself and need not be added from outside to low salt.

In Japanese Publication 02022122, seawater is selectively concentrated through an ion-exchange membrane and further concentrated in a vacuum evaporator to get desired level of NaCl and KCl in solution. Then the solution is cooled to separate a composite salt homogeneously containing both NaCl and KCl at desired ratios.

Whereas, the starting material of present invention is crude carnallite, obtained from low sulphate bittern, which is treated with calcium chloride to give desulphated bittern. The said desulphated bittern is solar evaporated in crystallizers, facilitated by high MgCl₂ concentration in bittern, to produce a solid mixture of NaCl and carnallite. This mixture is treated with water to produce low sodium salt. The resulting low sodium salt is dried and treated with additives to give free flowing properties. Moreover, the subsequent processing of the crude carnallite to yield low sodium salt is carried out under ambient conditions using simple decomposition with water.

The main objective of US Patent 3099528 is to produce pure KCl via sylvinitic obtained from crude carnallite. Producing crude carnallite from low sulphate brine by treating with CaCl₂ is not novel. The key issue is to carry out the desulphatation in a cost-effective manner. In the cited patent, calcium chloride used for desulphatation of brine is produced by passing heavy gypsum slurry to an ion-exchange system utilizing cationic exchange resin in its hydrogen form. This exchange must be carried out at elevated temperature. In present invention, distiller waste of the soda ash industry is utilized for the desulphatation, which is carried out directly in salt pans under ambient conditions. Moreover, Distiller waste contains NaCl along with CaCl₂ and this NaCl can, therefore, be recovered in the product of the invention.

The focus of GB Patent 1142901 and US Patent 3536444 are on preparation of KCl via crude carnallite whereas the novelty of the present invention is on utilization of the carnallite decomposed

WO 03/064323

PCT/IN02/00018

18

product comprising NaCl and KCl directly as low sodium edible salt. As for the method for production of crude carnallite, there is indeed novelty in the prior art in as much as no calcium chloride is required to produce carnallite even though the brine may have higher sulphate levels. Generation of concentrate MgCl₂ requires extremely difficult process of evaporation nearly to dryness. Whereas, in present invention, use of Distiller waste allows carnallite to be obtained directly from the desulphated bittern without recourse to external addition of magnesium chloride. In any event, the method of desulphation is as such not a principal claim of the present invention.

GB Patent 1500288 relates to reduction of sulphate content of an alkali chloride containing brine to as low as 2 gram/liter of sulphate by the addition of a stoichiometric excess of CaCl₂ while maintaining the brine's pH from 7 to 9 by HCl addition in temperature range of 30°C to 50°C. The application discussed does not involve salt or carnallite crystallization. The only overlap with the present invention is the use of calcium chloride for desulphation. As such the present invention does not claim any novelty in the use of calcium chloride for desulphation except to claim cost-effective desulphation through the use of Distiller waste.

The present invention should be viewed in the context of the prior art for manufacture of low sodium salt and not from the perspective of manufacturing process for carnallite. It is to illustrate the simplicity and cost-effectiveness of the present process vis-a-vis the prior art the method by which crude carnallite is formed is outlined in the claims.